SYNTHESIS AND CHARACTERIZATION OF TRANSITION METAL(II) COMPLEXES WITH CARBOHYDRAZONE/HYDRAZONE LIGANDS

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This project is submitted in partial fulfilment of the requirements for the
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DECLARATION

No portion of the work referred to this report has been submitted in support of an application for another degree of qualification of this or any other university of institution of higher learning.

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Synthesis and Characterization of Transition Metal(II) Complexes with Carbohydrazone/Hydrazone Ligands

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ABSTRACT

Four transition metal(II) complexes of each carbohydrazone-*bis*(2-hydroxynaphthaldehyde) (**1**) and pyridine-2-carboxaldehyde isonicotinichydrazone (**2**) ligands have been synthesized and characterized by CHN analyses, FTIR and UV-Visible spectral studies. All transition metal(II) complexes of carbohydrazone/hydrazone ligands have been analyzed by determining their molar conductivity. Two carbohydrazone/hydrazone ligands and their respective Co(II) complexes have also been characterized by ^{1}H NMR spectral study. All transition metal(II) complexes exhibited non electrolytic properties in nature. Spectral studies indicated both of the carbohydrazone/hydrazone ligands (**1**-**2**) acted as dinegative tridentate fashion towards the transition metal(II) ions. The proposed structures of the transition metal(II) complexes have been deduced on the basis of elemental analyses and spectral studies. Therefore, a four coordinated molecular structure has been proposed for the synthesized transition metal(II) complexes.

Key words: Transition metal(II) complexes; carbohydrazone-*bis*(2-hydroxynaphthaldehyde); pyridine-2-carboxaldehyde isonicotinichydrazone; spectral studies.

ABSTRAK

*Empat kompleks logam(II) peralihan daripada setiap karbohidrazida-bis(2-hidroksinaftaldehida) (**1**) dan piridin-2-karboaldehida isonikotinikhidrazida (**2**) ligan telah disintesis dan dicirikan dengan menggunakan teknik infra merah, cahaya ultra lembayung-tampak dan analisis elemen. Semua kompleks kepada kedua-dua ligan akan dicirikan dengan menentukan molar konduktiviti. Kedua-dua ligan dan kompleks Co(II) kepada kedua-dua ligan telah dicirikan dengan teknik ^{1}H NMR. Semua kompleks bersifat bukan electrolit secara semulajadi. Data-data spektra menunjukkan bahawa kedua-dua ligan (**1**-**2**) bertindak sebagai sebagai dinegatif tridentat dalam kompleks logam(II) peralihan. Maka, struktur molekul dengan empat koordinat telah dicadangkan untuk kesemua kompleks logam(II) peralihan yang telah disintesis dengan kedua-dua ligan tersebut.*

Kata kunci: Kompleks logam(II) peralihan; karbohidrazida-bis(2-hidroksinaftaldehida); piridin-2-karboaldehida isonikotinikhidrazida; kajian spektroskopik.

1.0 Introduction

1.1 Carbohydrazone/hydrazone ligands and their transition metal(II) complexes

Carbohydrazone/hydrazone ligand is an important compound which contains –NH-N=C- functional group. It is formed when an aldehyde or a ketone react with primary amine through condensation reaction. The carbohydrazone/hydrazone ligands have potential to act as electron pair donor, flexible, high chelating capability and able to coordinate either in keto or enol form. Hence, carbohydrazone/hydrazone ligand has variety of applications such as hole transporting agents in organic layer photo conductors, in pharmaceutical industry as drugs for treatment of cancer, schizophrenia and leprosy. Besides, it is useful in synthetic and industrial chemistry (Mishra *et al*., 2007).

The oxidation number of transition metal(II) ion is +2. Generally, transition metal(II) complexes involved in most of the chemical and biological catalytic activities (Pouralimardan *et al*., 2007) as well as anti-tumor activities (Yin *et al*., 2007).

1.2 Objectives

The objectives of the research are:

1.2.1 to synthesize two carbohydrazone/hydrazone ligands and their transition metal(II) complexes of [Co(II), Cu(II), Ni(II) and Fe(II)].

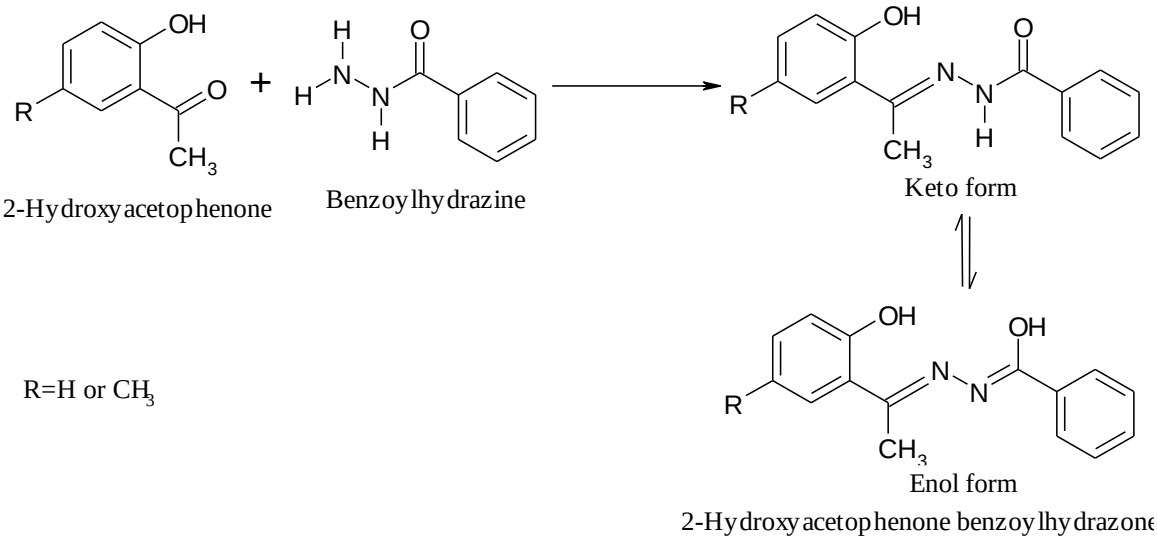
1.2.2 to characterize carbohydrazone/hydrazone ligands and their transition metal(II) complexes of [Co(II), Cu(II), Ni(II) and Fe(II)] by CHN analyses, molar conductivity, UV-Visible, FTIR and ^{1}H NMR spectral analyses.

1.2.3 to determine the molar conductance values of the synthesized transition metal(II) complexes.

2.0 Literature Review

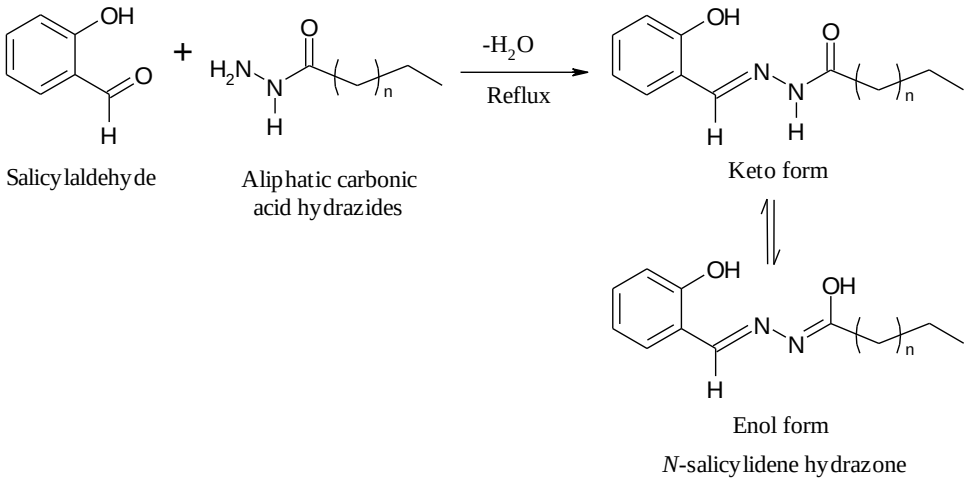
2.1 Synthesis of carbohydrazone/hydrazone ligands

2-Hydroxyacetophenone benzoylhydrazone obtained from the condensation reaction of benzoylhydrazine and 2-hydroxyacetophenone (Ghosh *et al*., 2007) as shown in Scheme 1. There are some medicinal properties for the vanadium complexes of the hydrazone ligand such as insulin-mimetic, anticancer, antitumor and antifungal or antibacterial activities.



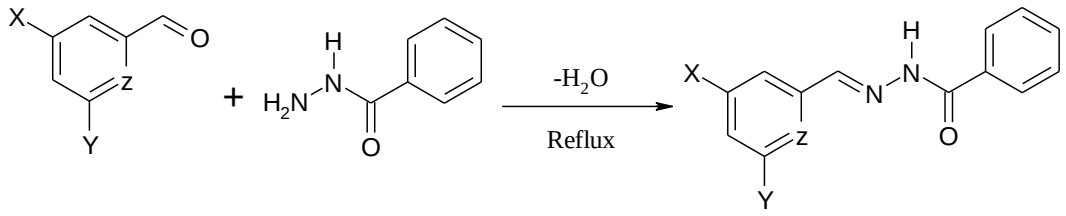
Scheme 1: Synthesis of 2-hydroxyacetophenone benzoylhydrazone

Another type of *N*-salicylidene hydrazone ligand was synthesized through the condensation reaction of salicylaldehyde and aliphatic carbonic acid hydrazides (Nica *et al*., 2007) as shown in Scheme 2. This hydrazone ligand was important in medicinal area.



Scheme 2: Synthesis of *N*-salicylidene hydrazone

Another important hydrazone ligands namely salicylaldehyde benzhydrazone and pyridine-2-carbaldehyde benzhydrazone. Salicylaldehyde benzhydrazone was derived from the condensation reaction of benzhydrazide and salicylaldehyde. While, pyridine-2-carbaldehyde benzhydrazone was derived from the condensation reaction of benzhydrazide and pyridine-2-carbaldehyde (Pouralimardan *et al*., 2007) as shown in Scheme 3.

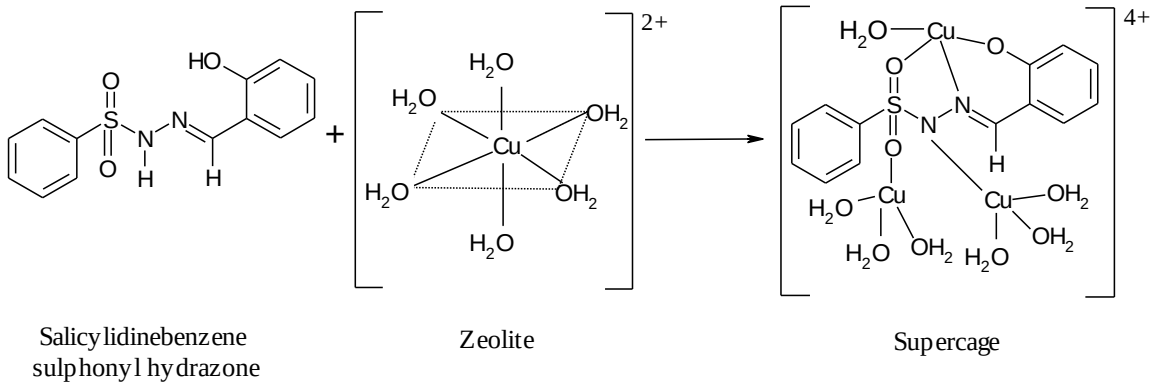


X=H or Br
Y=OCH_3, OH or H
Z=C-OH or N

Scheme 3: Synthesis of salicylaldehyde benzhydrazone and pyridine-2-carbaldehyde benzhydrazone

2.2 Transition metal(II) complexes with carbohydrazone/hydrazone ligands

Zeolite-encapsulated copper(II) hydrazone complex or simply namely as supercage was derived from the condensation reaction of salicylidinebenzenesulphonyl hydrazone with zeolite (Ahmed, 2007) as shown in Scheme 4. Copper(II) complexes were characterized by X-ray. Hence, the copper(II) complexes involved in applications of chromotropism, size and shape, selective catalysis, gas separation and purification, electro and photocatalysis.



Scheme 4: Synthesis of supercage

N-(*S*)-2-(6-methoxylnaphthyl)-propanoyl-*N*'-(2-hydroxylbenzylidene) hydrazone was coordinated to copper(II) salts (Wu *et al*., 2007) as shown in Figure 1. Salicylaldehyde-acylhydrazone Schiff base and coppper(II) complexes exhibit a wide spectrum of biological which can specially cleave the DNA.

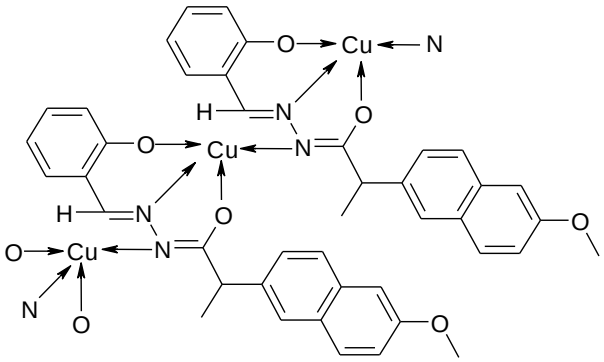


Figure 1: *N*-(*S*)-2-(6-methoxylnaphthyl)-propanoyl-*N*'-(2-hydroxylbenzylidene) hydrazone coordinated to copper(II) ions

Another important coordination compound was *trans,trans,trans-bis*(triphenylphosphine) *bis*(aroyl hydrazonato) ruthenium(II) complex derived from aroyl hydrazones (Mishra *et al*., 2007) as shown in Figure 2. The aroyl hydrazones involved in many application such as hole transporting agents in organic layer photo conductors, pharmaceutical industry, drugs for treatment (of cancer, schizophrenia and leprosy) and uses in synthetic and industrial chemistry.

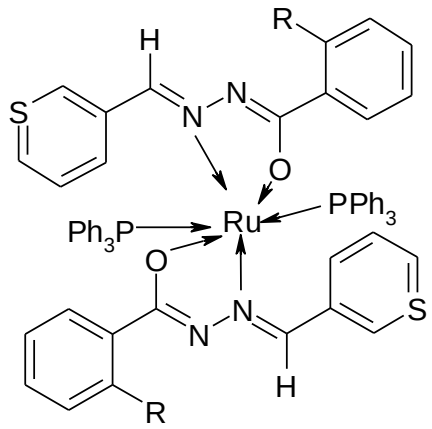


Figure 2: *Trans,trans,trans-bis*(triphenylphosphine) *bis*(aroyl hydrazonato) ruthenium(II) complexes

3.0 Material and Methodologies

3.1 Experimental

The research was carried out in the Inorganic Research Laboratory at Universiti Malaysia Sarawak (UNIMAS). All the chemicals were purchased from Fluka, Aldrich or J. T. Baker. All the solvents were purified and dried by standard methods (Armego *et al*., 1996).

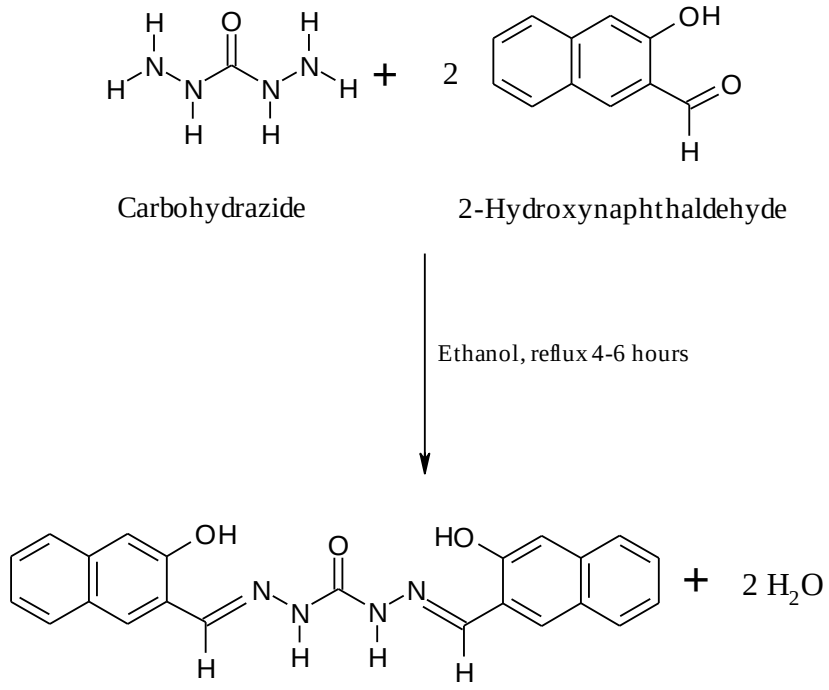
3.2 Measurements

Infrared spectra of carbohydrazone/hydrazone ligands and their transition metal(II) complexes were recorded as KBr disc using Perkin Elmer Spectrum GX Fourier-Transform Infrared Spectrometer in range of 4000-370 cm^{-1}. Besides, the electronic absorption spectra of the carbohydrazone/hydrazone ligands and their transition metal(II) complexes were recorded using Perkin Elmer Lamda 25 Spectrometer. While the proton (^1H) NMR spectra of the carbohydrazone/hydrazone ligand and its Co(II) complex were recorded using Jeol 500 MHz Spectrometer in DMSO–d_6. On the other hand, the molar conductance of the transition metal(II) complexes were recorded using Jenway 4320 conductivity meter. The melting point of carbohydrazone/hydrazone ligands and their transition metal(II) complexes were measured using the Stuart MP3 analyzer.

3.3 Synthesis of ligand (1) and its transition metal(II) complexes (3-6)

3.3.1 Synthesis of $[C_{23}H_{18}N_4O_3]$ (1)

A mixture of carbohydrazide (0.901 g, 0.010 mol) and 2-hydroxynaphthaldehyde (3.444 g, 0.020 mol) in 20 mL of absolute ethanol were stirred and heated under reflux for 4-6 hours. The reaction mixture was allowed to cool to room temperature for 30 minutes. The milky yellow precipitate formed was filtered off and washed several times using absolute ethanol. The milky yellow precipitates were recrystallized from hot absolute ethanol and dried in vacuo over silica gel. **1:** Yield: 3.35 g, 84%.



Scheme 5: Proposed structure of ligand $[C_{23}H_{18}N_4O_3]$ (**1**)

3.3.2 Synthesis of [Co($C_{23}H_{16}N_4O_3$)(H_2O)] (3)

Co(II) complex (**3**) was obtained by the direct reaction of ligand (**1**) with cobalt(II) chloride hexahydrate in 1:1 mole ratio (Pouralimardan *et al*., 2007). Ligand (**1**) (0.398 g, 0.001 mol) was dissolved in absolute methanol (10 mL). Then, cobalt(II) chloride hexahydrate (0.238 g, 0.001 mol) in methanol (10 mL) was added dropwise using a dropper. The resulting solution was refluxed for 4-6 hours and allowed to cool to room temperature for 30 minutes. The light brown precipitate was collected by filtration and washed several times using absolute methanol. The light brown precipitates were recrystallized from hot absolute ethanol and dried in vacuo over silica gel. **3:** Yield: 0.38 g, 80%.

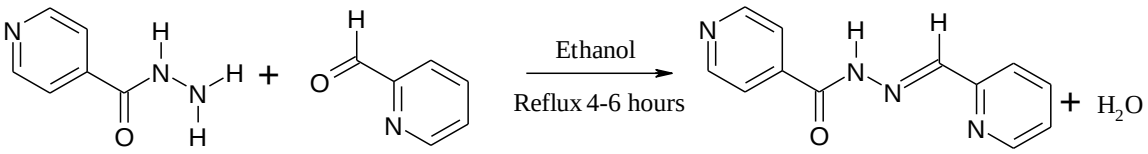
3.3.3 Synthesis of transition metal(II) complexes (4-6)

Transition metal(II) complexes (**4-6**) were synthesized using the same procedure as shown in synthesis of Co(II) complex (**3**). The reaction was 1:1 mole ratio. Transition metal(II) salts used are copper(II) chloride-2-hydrate, nickel(II) chloride hexahydrate and iron(II) chloride hexahydrate, respectively. **4:** Yield: 0.33 g, 67%; **5:** Yield: 0.28 g, 58%; **6:** Yield: 0.33 g, 70%.

3.4 Synthesis of ligand (2) and its transition metal(II) complexes (7-10)

3.4.1 Synthesis of $[C_{12}H_{10}N_4O]$ (2)

A mixture of isonicotinichydrazide (1.371 g, 0.010 mol) and pyridine-2-carboxaldehyde (1.071 g, 0.010 mol) in 20 mL of absolute ethanol were stirred and heated under refluxed for 4-6 hours. The reaction mixture was allowed to cool to room temperature for 30 minutes. The milky brown precipitate formed was filtered off and washed several times using absolute ethanol. The milky brown precipitates were recrystallized from hot absolute ethanol and dried in vacuo over silica gel. **2:** Yield: 1.71 g, 76%.



Isonicotinichydrazide Pyridine-2-carboxaldehyde

Pyridine-2-carboxaldehyde Isonicotinichydrazone

Scheme 6: Proposed structure of ligand $[C_{12}H_{10}N_4O]$ (**2**)

3.4.2 Synthesis of [Co($C_{12}H_9N_4O$)(H_2O)] (7)

Co(II) complex (**7**) was obtained by the direct reaction of ligand (**2)** with cobalt(II) chloride hexahydrate in 1:1 mole ratio (Pouralimardan *et al*., 2007). Ligand (**2**) (0.226 g, 0.001 mol) was dissolved in absolute methanol (10 mL). Then, cobalt(II) chloride hexahydrate (0.238 g, 0.001 mol) in methanol (10 mL) was added dropwise using a dropper. The resulting solution was refluxed for 4-6 hours and allowed to cool to room temperature for 30 minutes. The green precipitate was collected by filtration and washed several times using absolute methanol. The green precipitates were recrystallized from hot absolute ethanol and dried in vacuo over silica gel. **7:** Yield: 0.35 g, 78%.

3.4.3 Synthesis of transition metal(II) complexes (8-10)

Transition metal(II) complexes (**8-10**) were synthesized using the same procedure as shown in synthesis of Co(II) complex (**7**). The reaction was 1:1 mole ratio. Transition metal(II) salts used are copper(II) chloride-2-hydrate, nickel(II) chloride hexahydrate and iron(II) chloride hexahydrate, respectively. **8:** Yield: 0.32 g, 72%; **9:** Yield: 0.29 g, 79%; **10:** Yield: 0.25 g, 71%.

4.0 Results and discussion

Carbohydrazone ligand (**1**) was obtained from the condensation reaction of carbohydrazide and 2-hydroxynaphthaldehyde in absolute ethanol with 1:2 mole ratio. The reaction of methanolic solution of carbohydrazone-*bis*(2-hydroxynaphthaldehyde) ligand (**1**) with Co(II), Cu(II), Ni(II) and Fe(II) ions yielded the transition metal(II) complexes (**3**-**6**). Transition metal(II) complexes (**3**-**6**) were prepared by the general equation as shown in equation 1.

$$MCl_2{\cdot}nH_2O + [C_{23}H_{18}N_4O_3]\ (\mathbf{1}) \xrightarrow[\text{Reflux 4-6 hrs}]{\text{Abs. MeOH}} [M(C_{23}H_{16}N_4O_3)(H_2O)] \qquad (1)$$

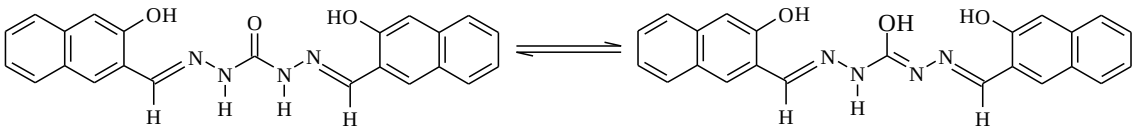
$MCl_2{\cdot}nH_2O$ = $CoCl_2{\cdot}6H_2O$, $CuCl_2{\cdot}2H_2O$, $NiCl_2{\cdot}6H_2O$ or $FeCl_2{\cdot}6H_2O$

Hydrazone ligand (**2**) was obtained from the condensation reaction of isonicotinichydrazide and pyridine-2-carboxaldehyde in absolute ethanol with 1:1 mole ratio. The reaction of methanolic solution of pyridine-2-carboxaldehyde isonicotinichydrazone ligand (**2**) with Co(II), Cu(II), Ni(II) and Fe(II) ions gave the transition metal(II) complexes (**7**-**10**). Transition metal(II) complexes (**7**-**10**) were prepared by the general equation as shown in equation 2.

$$MCl_2{\cdot}nH_2O + [C_{12}H_{10}N_4O]\ (\mathbf{2}) \xrightarrow[\text{Reflux 4-6 hrs}]{\text{Abs. MeOH}} [M(C_{12}H_9N_4O)(H_2O)] \qquad (2)$$

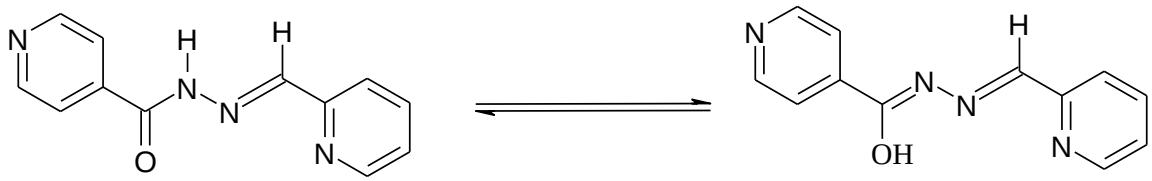
$MCl_2{\cdot}nH_2O$ = $CoCl_2{\cdot}6H_2O$, $CuCl_2{\cdot}2H_2O$, $NiCl_2{\cdot}6H_2O$ or $FeCl_2{\cdot}6H_2O$

The proposed structure of the carbohydrazone/hydrazone ligands (**1**-**2**) are shown in Figure 3 and Figure 4. Both carbohydrazone/hydrazone ligands (**1**-**2**) acted as dinegative tridentate ligands which are capable to form transition metal(II) complexes with various transition metal(II) ions. Both carbohydrazone/hydrazone ligands (**1**-**2**) have an amide group (–NH–C=O), so, they can exhibit keto (1a) and enol (1b) tautomerism (Figure 3-4) in solution.



1a **1b**

Figure 3: Proposed structure of the ligand (**1**) in keto (**1a**) and enol (**1b**) form



1a **1b**

Figure 4: Proposed structure of the ligand (**2**) in keto (**1a**) and enol (**1b**) form

The synthesized carbohydrazone/hydrazone ligands and their transition metal(II) complexes are stable at room temperature. Both ligands (**1**-**2**) were soluble in common organic solvents but their transition metal(II) complexes are generally soluble in very polar solvents like DMF and DMSO. Physical properties and elemental analyses of carbohydrazone/hydrazone ligands (**1**-**2**) and their transition metal(II) complexes (**3**-**10**) are given in Table 1.

The molar conductance values of transition metal(II) complexes (**3-10**) with $1x10^{-4}$ M in MeOH solvent at room temperature are shown in Table 2. The low molar conductance values (6-24 Ω^{-1} cm^2 mol^{-1}) indicating non electrolytic nature for all the transition metal(II) complexes (**3-10**).

The probable structure characterization of the carbohydrazone/hydrazone ligands and their transition metal(II) complexes are confirmed by IR and UV-Visible spectral studies.

Table 1: Physical properties and elemental analyses of carbohydrazone/hydrazone ligands (**1**-**2**) and their transition metal(II) complexes (**3**-**10**)

Compounds	Colour	Yield (%)	Melting point (°C)	Found (Calculated) %		
				C	H	N
$[C_{23}H_{18}N_4O_3]$ (**1**)	Milky yellow	84.01	290-293	69.30 (69.34)	4.58 (4.55)	14.08 (14.06)
$[C_{12}H_{10}N_4O]$ (**2**)	Milky brown	75.60	160-164	63.67 (63.71)	4.50 (4.46)	24.76 (24.77)
$[Co(C_{23}H_{16}N_4O_3)(H_2O)]$ (**3**)	Light brown	80.34	294-296	58.33 (58.36)	3.85 (3.83)	11.82 (11.84)
$[Cu(C_{23}H_{16}N_4O_3)(H_2O)]$ (**4**)	Dark green	66.95	287-289	57.76 (57.80)	3.81 (3.79)	11.70 (11.72)
$[Ni(C_{23}H_{16}N_4O_3)(H_2O)]$ (**5**)	Brownish yellow	58.13	296-300	58.42 (58.39)	3.83 (3.84)	11.81 (11.84)
$[Fe(C_{23}H_{16}N_4O_3)(H_2O)]$ (**6**)	Deep green	70.21	264-267	58.77 (58.74)	3.85 (3.86)	11.92 (11.91)
$[Co(C_{12}H_9N_4O)(H_2O)]$ (**7**)	Green	78.41	280-283	47.74 (47.70)	3.65 (3.67)	18.57 (18.54)
$[Cu(C_{12}H_9N_4O)(H_2O)]$ (**8**)	Dark green	72.72	258-259	47.02 (46.98)	3.59 (3.61)	18.24 (18.26)
$[Ni(C_{12}H_9N_4O)(H_2O)]$ (**9**)	Light green	79.85	318-320 (d)	47.73 (47.74)	3.65 (3.67)	18.60 (18.56)
$[Fe(C_{12}H_9N_4O)(H_2O)]$ (**10**)	Black	70.82	269-271 (d)	48.22 (48.19)	3.69 (3.71)	18.77 (18.73)

d=decompose

Table 2: Molar conductance values for the transition metal(II) complexes (**3-10**) with carbohydrazone/hydrazone ligands (**1-2**)

Compounds	**Molar conductance, Λm^a (Ω^{-1} cm^2 mol^{-1})**
$[Co(C_{23}H_{16}N_4O_3)(H_2O)]$ (**3**)	9
$[Cu(C_{23}H_{16}N_4O_3)(H_2O)]$ (**4**)	10
$[Ni(C_{23}H_{16}N_4O_3)(H_2O)]$ (**5**)	10
$[Fe(C_{23}H_{16}N_4O_3)(H_2O)]$ (**6**)	6
$[Co(C_{12}H_9N_4O)(H_2O)]$ (**7**)	24
$[Cu(C_{12}H_9N_4O)(H_2O)]$ (**8**)	11
$[Ni(C_{12}H_9N_4O)(H_2O)]$ (**9**)	18
$[Fe(C_{12}H_9N_4O)(H_2O)]$ (**10**)	18

[a] in MeOH solvent at room temperature ($1x10^{-4}$ M)